

## VII.F.5 Fuel Processing R&D

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*Start Date: October 1, 2004*

*Projected End Date: September 30, 2006*

### Objectives

- Study reforming of propane
  - Define reaction kinetics and operating conditions
  - Define and resolve challenges with minor components and contaminants
- Develop a strategy for designing a single-stage water-gas-shift (WGS) reactor that will incorporate temperature control and gas separation

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Cost (use of precious metals, low activity of shift catalysts)
- I. Hydrogen Purification/Carbon Monoxide Cleanup

### Technical Targets

The catalytic reactor accounts for a major fraction of the fuel processor weight, volume, and cost. Developing a design strategy that can increase the space velocity by a factor of 5-10 will lead to a more compact and lower-cost fuel processor.

- Study propane reforming reaction kinetics and yields
  - Effect of reforming type (steam reforming, partial oxidation, autothermal reforming), operating parameters (temperature, space velocity, steam/carbon ratio), minor species (e.g., propylene, etc.)
- Develop a strategy (model) for a conceptual membrane reactor that combines separation ( $H_2$ , CO, or  $CO_2$ ) with temperature control in a WGS reactor
  - Produce reformat that contains less than 1% CO at the shift reactor exit
  - Implement strategy to operate at space velocities of 20,000  $hr^{-1}$  or more

### Approach

- Conduct reaction studies using micro-reactor to establish kinetics and product yields
- Identify catalyst and establish kinetic parameters
- Model the reactor, incorporating temperature control and membrane separation
- Confirm conversion using a preferred temperature profile in a laboratory reactor
- Validate model to benchmark achievable benefit and project improvements with membrane separation

## Accomplishments

- Established preferred operating regimes for propane reforming based on simplified models and thermodynamic equilibria
- Initiated steam reforming reaction studies
- Effect of temperature and space velocity
- Established kinetics for two types (dependent and independent of CO concentration) of catalyst for the WGS reactor and compared anticipated behavior
- Developed a shift reactor model using parallel plate geometry
- Modeled the reactor under adiabatic conditions and with isothermal and optimum temperature profiles
- Fabricated laboratory-scale reactor with integrated heat transfer
- Initiated experiments to validate model predictions

## Future Directions

- Fabricate micro-reactor for propane partial oxidation reaction studies
- Conduct experiments to evaluate effect of process conditions to validate model
- Expand WGS reactor model to include combination of heat transfer and separation
- Demonstrate laboratory-scale single-stage WGS reactor

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## Introduction

Propane is widely available in urban and rural settings and as such is an attractive fuel for distributed fuel cell power. Reformers for these systems will benefit from public domain disclosure of reformer kinetics and performance as it pertains to preferred catalyst and reactor combinations. The fuel processors used by these fuel cell systems typically include a WGS reactor, an essential component in the fuel processing train. The size, weight, and cost of this component have been attributed to the slow kinetics that control the conversion at low CO concentrations.

This project studies the reforming kinetics and product yields achievable with a state-of-the-art reforming catalyst, under conditions that range from steam reforming (SR) to partial oxidation reforming to autothermal reforming. The peculiarities of propane, such as the presence of propylene, the sulfur content, etc., are being investigated with respect to their effects on product distribution, kinetics, and durability.

This project follows the reformer effluent (reformate) through the water-gas shift reactor, by undertaking the development of a strategy to help manufacturers design a single-stage WGS reactor,

using a combination of catalytic reaction, temperature control, and gas separation. Operating the shift reactor at space velocities greater than 20,000 per hour will lead to a compact fuel processor. The lower catalyst requirement may also lead to a cost reduction.

## Approach

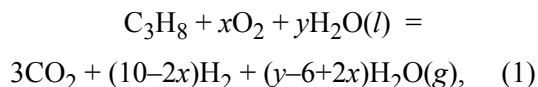
Initially, efficiency and thermodynamic calculations on the reforming reaction were conducted to define the preferred operating domain, which was then followed by the setup of the micro-reactor apparatus. Experiments will be conducted to establish the kinetics and the effect of operating conditions on product yields.

The WGS reactor study commenced with the establishment and comparison of the kinetics of two classes of catalysts—where the reaction rate is (1) dependent and (2) independent of CO concentration. The kinetic correlations were used in a generic model to predict the conversion during adiabatic, isothermal, or optimized temperature profile operation. A laboratory reactor is being used to study the desired combination of heat transfer and catalytic reaction, and will be used to validate the model. The model will then be expanded to include gas separation.

## Results

### Propane Reforming

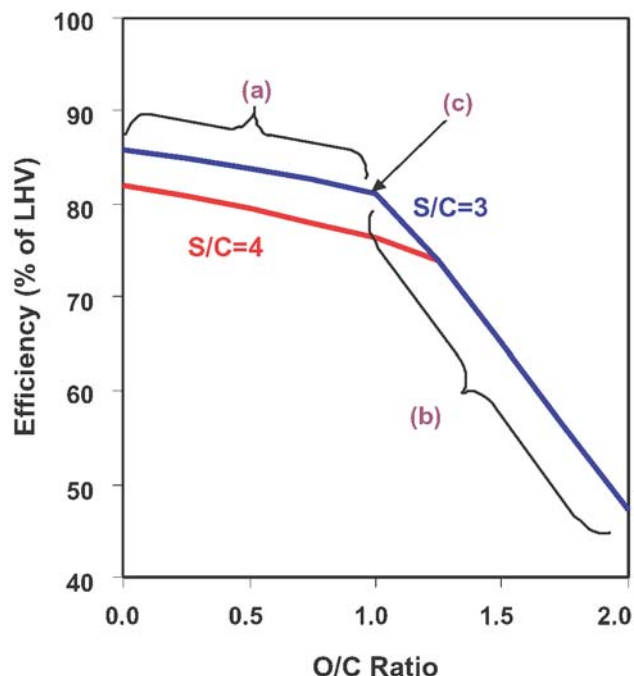
The overall reforming reaction for propane can be represented by the equation:



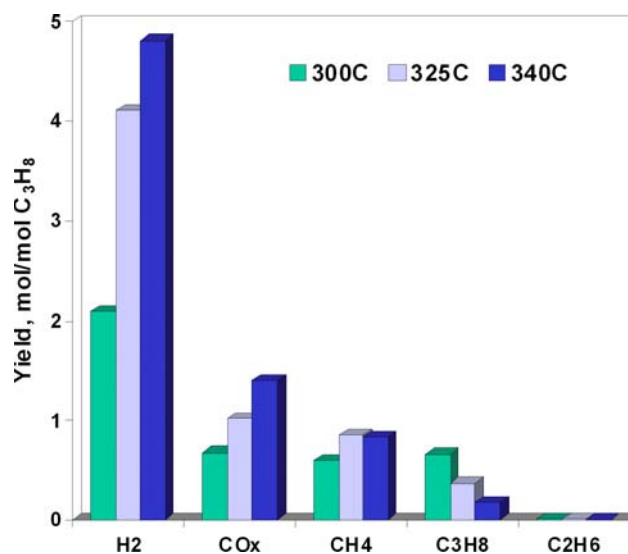
where,  $x$  and  $y$  are the oxygen-to-fuel and water-to-fuel molar ratios, respectively. The water on the right side of the equation represents any excess water that may be used in the process. Note that while the reactant water is assumed to be a liquid, the water in the exhaust gas is in the vapor form. The heat of reaction depends upon  $x$  and  $y$ . Thus at  $x = 0$ , the reaction corresponds to the SR reaction and is strongly endothermic. Adding oxygen generates heat, reaching thermoneutrality ( $\Delta H = 0$ ) before becoming exothermic at even higher values of  $x$ .

The hydrogen yield from the idealized reaction above is a function of the oxygen-to-carbon atomic ratio ( $\text{O/C} = 2x/3$ ), and the steam-to-carbon ratio, ( $\text{S/C} = y/3$ ). For the purposes of this analysis, the efficiency of this idealized reforming process has been defined as the lower heating value (LHV) of hydrogen as a percentage of the total energy input. Besides the propane reacting (Equation), the input energy also includes any energy needed (when the reaction is endothermic) for heat balance. Figure 1 plots the relationship between efficiency and the O/C ratio for  $\text{S/C} = 3$  and  $\text{S/C} = 4$ . The general trend is that with increasing oxygen input, less hydrogen is produced, decreasing the process efficiency. The region (a) of the curves in the figure represents the endothermic operating conditions. The knee represents the thermoneutral point. In Region (b), where the O/C is still higher, energy is lost as sensible heat with the products, and the efficiency drops sharply. The trends suggest that the process should be operated to the left of (c).

An experimental micro-reactor system has been set up to study the kinetics and product yields during SR reactions. The reactor has been tested with ~5 g of granular (20-40 mesh) catalyst (rhodium on  $\text{La/Al}_2\text{O}_3$ ). Figures 2 and 3 show the effects of temperature and space velocity on the product yields, respectively.



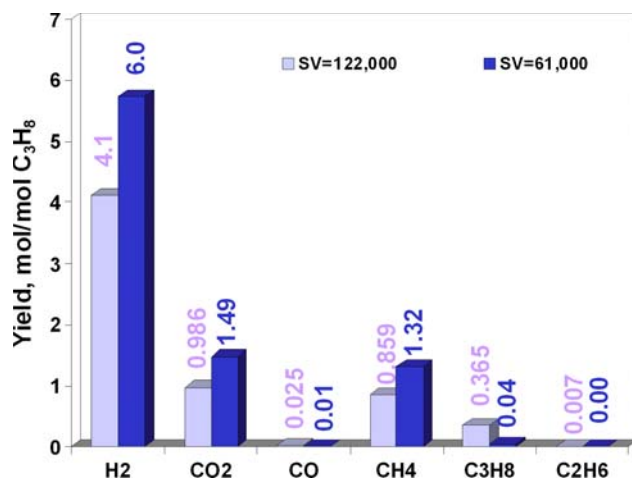
**Figure 1.** Effect of the O/C on Propane Reforming Efficiency



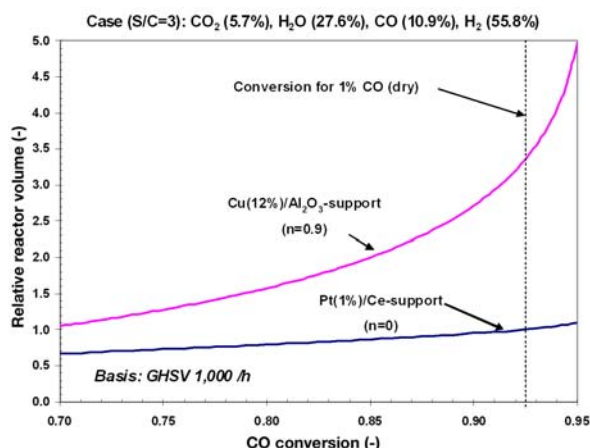
**Figure 2.** Effect of Temperature on Product Yields from the SR of Propane (gas hourly space velocity [GHSV] = 122,000  $\text{hr}^{-1}$ ,  $\text{S/C} = 45$ )

### Water-Gas Shift Reactor

A review of literature data provided kinetic information for two types of WGS catalysts [1,2]. A copper catalyst ( $n \approx 1$ , i.e., first-order with respect to CO) and a platinum catalyst ( $n = 0$ , i.e., zero order with respect to CO) were compared for their ability



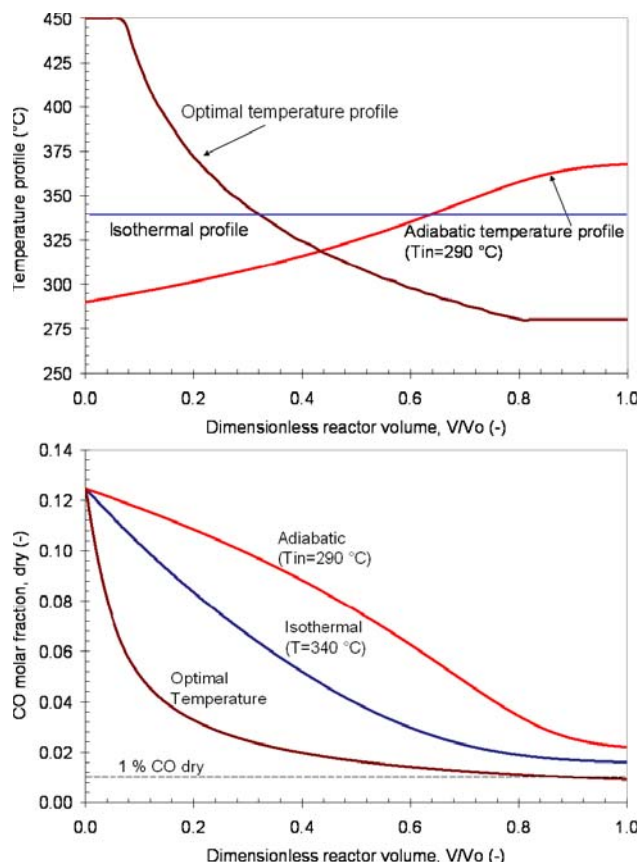
**Figure 3.** Effect of GHSV on the Product Yields from the SR of Propane ( $T = 325^{\circ}\text{C}$ ,  $S/C = 45$ )



**Figure 4.** Reactor Volumes Needed to Reduce CO from 10.9% to 1% Using a Copper Catalyst and a Platinum Catalyst.

to reduce CO in a reformat stream from 10.9% to 1%. Figure 4 shows the conversions achievable with each catalyst under adiabatic conditions. The platinum catalyst will achieve the desired conversion at a space velocity of  $1,000 \text{ hr}^{-1}$  or a relative reactor volume of 1. In contrast, the copper catalyst will require a reactor volume that is 3.4 times the volume of the platinum-loaded reactor.

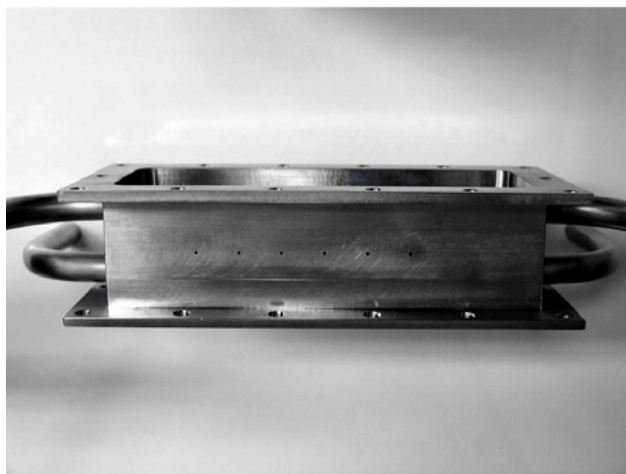
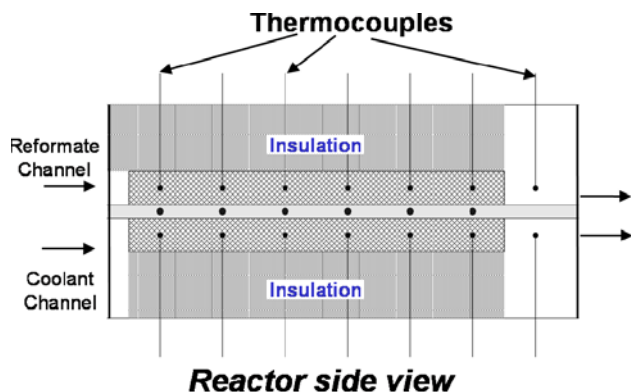
Shift reaction data available from the Argonne National Laboratory catalyst program were used to establish the kinetics of an advanced Pt-Re catalyst, a zero-order catalyst (w.r.t. CO). The kinetic expression was then used in a model to predict the temperature profiles and CO concentrations during



**Figure 5.** Temperature and CO Concentration Profiles for Adiabatic, Isothermal, and Optimal Temperature Operations of a WGS Reactor Using a Pt-Re/Ce Catalyst. Dimensionless Reactor Volume 1.0 =  $30,000 \text{ hr}^{-1}$ .

three operating modes: adiabatic, isothermal, and optimal. Figure 5 plots the temperatures and CO concentrations as a function of the dimensional reactor volume, where 1 is equivalent to a space velocity of  $30,000 \text{ hr}^{-1}$ . Only the reactor with the optimal temperature profile was able to reduce the CO concentration to 1%. The isothermal reactor at  $340^{\circ}\text{C}$  performed better than the adiabatic reactor with an inlet temperature of  $290^{\circ}\text{C}$ . The isothermal reactor achieved 1.7% CO while the adiabatic reactor could only reduce the CO to 2.2% at the same reactor volume.

To validate the model, an experimental reactor designed to process up to 4 L/min of dry reformat has been fabricated and loaded with the catalyst. Figure 6 shows a schematic and a photograph of the reactor. The experiments have been initiated. Simulations of the experimental reactor predict that



**Figure 6.** Schematic and Photograph of an Experimental WGS Reactor

the CO concentration profile should closely follow the optimal profile. With an inlet temperature of 375°C, the experimental unit is expected to reduce the CO level from 12.5% to 1% at a space velocity exceeding 20,000 hr<sup>-1</sup>. If experimentally confirmed, this would represent a significant reduction in shift

reactor volume compared with the state-of-the-art reactors, which operate in the 2,000-5,000 hr<sup>-1</sup> range.

### **Conclusions**

Simple process calculations have been conducted to establish the preferred operating conditions for propane reforming. An experimental reactor has been set up and SR reactions have been initiated. Data obtained have shown the effect of temperature and space velocity on product yields.

The kinetics of the WGS reaction have been used to compare the performance of two types of catalysts. Catalysts with a zero-order reaction rate with respect to CO concentration are favored for approaching low CO levels. An ideal temperature and concentration profile has been defined for a Pt-Re catalyst. A model of a single-stage WGS reactor predicts that CO conversion from 12.5% to 1% may be achievable at space velocities exceeding 20,000 hr<sup>-1</sup>, using only temperature control. An experimental reactor has been set up and is being tested for model validation.

### **References**

1. Qi, X., and Flytzani-Stephanopoulos, M., "Activity and stability of Cu-CeO<sub>2</sub> catalysts in high-temperature water-gas shift for fuel cell applications," *Industrial and Engineering Chemistry Research*, **43**, 3055-3062, 2004
2. Wheeler, C., Jhalani, A., Klein, E.J., Tummala, S., and Schmidt, L., "The water-gas shift reaction at short contact times," *Journal of Catalysis*, **223**, 191-199, 2004.